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13. ABSTRACT (Mezimum 200 words)

The major accomplishment of this grant has been to develop techniques for the in situ preparation of high-T_c superconducting films involving the use of ozone-assisted molecular beam epitaxy. The techniques are generalizable to the growth of trilayer and multilayer structures. Films of both the DyBa₂Cu₃O_{7-x} and YBa₂Cu₃O_{7-x} compounds as well as the La_{2-x}Sr_xCuO₄ compound have been grown on the usual substrates, SrTiO3, YSZ, MgO, and LaAlO3, as well as on Si substrates without any buffer layer. A bolometer has been fabricated on a thermally isolated SiN substrate coated with YSZ, an effort carried out in collaboration with Honeywell Inc. The deposition process facilitates the fabrication of very thin and transparent films creating new opportunities for the study of superconductor-insulator transitions and the investigation of photo-doping with carriers of high temperature superconductors. In addition to a thin film technology, a patterning technology has been developed. Trilayer structures have been developed for FET devices and tunneling junctions. Other work includes the measurement of the magnetic properties of bulk single crystal high temperature superconductors, and in collaboration with Argonne National Laboratory, measurement of electric transport properties of Tl-based high-Tc films.

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Final Report

HIGH TEMPERATURE SUPERCONDUCTING COMPOUNDS

AFOSR GRANT NO. 87-0372

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SUMMARY

The major accomplishment of this grant (AFOSR-87-0372) has been to develop a technique for the in situ preparation of high-Tc superconducting films involving the use of ozone-assisted molecular beam epitaxy. The method is highly reliable and reproducible. The procedures seem to be generalizable to the extent that high quality trilayer and multilayer structures which would be useful scientifically and technologically are possible. With this approach it has been possible to grow films of both the DyBa₂Cu₃O_{7-x} and YBa₂Cu₃O_{7-x} compounds as well as the La_{2-x}Sr_xCuO₄ compound. In addition to the process working with the usual substrates, SrTiO3, YSZ, MgO, and LaAlO₃, it has been possible to deposit films on Si substrates without any buffer layer. A bolometer has been successfully fabricated on a thermally isolated SiN substrate coated with YSZ. The latter effort was carried out in collaboration with Honeywell Inc. The deposition process also facilitates the fabrication of very thin and transparent films with relatively high transition temperatures. This has created new opportunities for the study of superconductor-insulator transitions and the investigation of photo-doping with carriers of high temperature superconductors. At the time of the completion of the grant a major effort at the fabrication of trilayer structures consisting of two high-T_c films separated by an insulating layer was under way. This was being carried out using a Perkin-Elmer molecular beam epitaxy machine designed for growing high-T_c materials. In addition to a thin film technology, a patterning technology has been developed for the trilayer work. These trilayer structures are being developed as FET devices and tunneling junctions.

Another important activity supported by this grant has been the measurement of the magnetic properties of bulk polycrystalline and single crystal high temperature superconductors. These investigations have revealed important features of flux pinning and anisotropy in these materials. Other major areas of effort have involved the development of a low temperature scanning tunneling microscope for the investigation of the surfaces of high- T_c superconductors, and the development of spherical target sputtering as a means of growing high- T_c films. In collaboration with Argonne National Laboratory, electrical transport above and in the vicinity of the transition of T_c films has been investigated. This work has revealed features of the fluctuations in the normal state and of the Kosterlitz-Thouless character of the transition.

I. INTRODUCTION

This report describes the results of research during the period 1 September 1987 to 30 September 1992 conducted under AFOSR Grant No. 87-0372. The work is concerned with high-T_c superconducting compounds. These materials first attracted worldwide attention more than five years ago. The efforts supported under the grant are directed at both the bulk and thin film forms of these oxides with the ultimate objective of elucidating the underlying mechanism(s) for the superconductivity of these materials as well as developing processes and structures of technological significance.

The new high-T_c materials, and the prospect of future discoveries involving ultrahigh transition temperature superconductivity, have greatly broadened interest in superconductivity in both the engineering and scientific communities. Superconducting materials may be offered as a solution to a variety of problems in areas of technology hitherto abandoned to more conventional materials. The prospect of practical superconductivity at liquid nitrogen temperatures (and perhaps higher) could have an enormous impact on a variety of industrial and military technologies in areas relating to energy, electronics and information processing.

It is clear that future technological success is related to abilities to control the chemical composition and morphology and perhaps to the development of the capability to fabricate thin films of prescribed morphology and chemical composition. Although most of the advances in the limiting values of superconducting parameters have come from empirical discoveries associated with highly Edisonian fabrication efforts, optimization of the properties may result from theoretical modeling which should point the way towards future improvements in such properties. The efforts involved in preparing samples of sufficient quality to test theoretical models and answer other scientific questions are closely related to those efforts needed for the development of materials adequate for superconducting technology.

The history of the past six years of research on high temperature superconductors demonstrates that a major ongoing technical challenge in the field, in addition to finding additional materials with even higher T_c 's, is the preparation of materials of exceptionally high quality. This is essential to facilitate the determination of intrinsic superconducting properties with a certain degree of confidence, thus facilitating the elucidation of the mechanism for high temperature superconductivity. These materials are also necessary if practical devices are to be realized.

Materials have been fabricated in both bulk and thin film form and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), scanning tunneling microscopy (STM) and atomic force microscopy (AFM). These studies have been correlated with investigations of macroscopic superconducting properties such as critical temperatures, transition widths, critical magnetic fields, the Meissner effect, and penetration depths. Techniques for the fabrication of thin films and structures have progressed to a point where the fabrication of planar tunneling junctions and proximity effect structures may actually be feasible in the short term.

II. SCIENTIFIC RESULTS

A. Preparation of High-T_c Films by Ozone-assisted Molecular Beam Epitaxy and Related Efforts: Early Efforts

This research grew out of a previous AFOSR program to develop techniques for the growth of film superconducting compounds by co-evaporation. The early efforts resulted in the synthesis of Y₂Ba₄Cu₈O_{20-x} films which were post-annealed (Berkley, et al., 1988a). It was then realized that YBa₂Cu₃O_{7-x} films could be prepared in situ without a post-anneal by using an ozone vapor jet as an oxygen source (Berkley, et al., 1988b). In both of these initial works a combination of electron beam and Knudsen vapor sources was employed for the various metallic constituents. It is clear that the use of a well-characterized oxidizing gas is very useful for the fabrication of high-T_c superconducting films. The details of these procedures were described in a comprehensive article published in the Review of Scientific Instruments (Berkley, et al., 1989a), and in a summary of an invited talk at an international conference on thin film technology held during the summer of 1991 (Achutharaman, 1991).

A major improvement on the process followed with the abandonment of electron beam sources for a configuration in which the elemental constituents were deposited entirely using Knudsen cells. Films of DyBa₂Cu₃O_{7-x} with transition temperatures as high as 89 K and with nominal thicknesses down to 35 Å were grown in situ using molecular beam epitaxy (MBE) employing ozone (Johnson, et al., 1990). The growth process, which was carried out at a substrate temperature of 700°C, was successful with a variety of substrates including SrTiO₃(100), SrTiO₃(110), LaAlO₃(100), MgO(100), and yttria stabilized zirconia (YSZ). The surfaces of these films could be imaged with an STM operating at 4.2 K, indicating a conducting surface even at low temperatures. Recently we have been able to grow films at a substrate temperature of 600°C directly onto Si substrates without any preconditioning. The best film to date prepared in this manner has an onset temperature of 90 K, and a zero resistance temperature of 70 K. This result implies that ozone-assisted MBE may be very valuable for the fabrication of hybrid semiconductor-superconductor devices.

A particularly interesting application of the above techniques was the fabrication of a high temperature superconducting microbolometer employing a DyBaCuO film deposited onto a silicon microstructure. This device was found to have a responsivity of 800V/W at 89 K and a response time of 1 ms (Stratton, et al., 1990).

B. Tunneling Junctions with High Temperature Superconductors

Work was begun towards the development of tunneling junctions and other heterostructures based on DyBaCuO. First it was discovered that superconducting DyBaCuO could be grown epitaxially on a buffer layer of Dy2O3. The latter was prepared in the vacuum chamber by simply closing the shutters on the Ba and Cu sources. Cross-sectional TEM revealed very sharp boundaries between the DyBaCuO and the underlying buffer layer. Then DyBaCuO-Dy2O3-DyBaCuO sandwiches were produced and examined by cross-sectional TEM. Again very sharp boundaries were formed, and the structure appeared as a monolithic epitaxial layer when examined using various microstructural characterization techniques. These results are extraordinarily encouraging for the production of tunneling junctions and heterostructures made from high temperature superconductors. The next step will be to implement patterning and produce sandwiches with thin barriers, which should permit tunneling studies to be carried out. This work was presented at the 1990 Applied Superconductivity Conference and appeared in the Proceedings of that meeting (Beauchamp, et al., 1991).

1. Epitaxial Multilayers: Early Work

Layered structures of DyBa₂Cu₃O_{7-x} and Dy₂O₃ grown on (100) and (110) oriented SrTiO₃ have been examined in cross section by TEM and energy dispersive spectroscopy (EDS) to determine the feasibility of fabricating tunneling junctions and other structures using these materials. The two materials exhibit a clear epitaxial relationship, resulting in heteroepitaxial growth of DyBa₂Cu₃O_{7-x} on Dy₂O₃. The interfaces between the two compounds are structurally sharp, but interdiffusion between the chemical constituents occurs. Nevertheless, these results are a strong indication that high quality high-T_c superconductor tunneling junctions can be fabricated in this system. The degree of perfection is such that it may also be possible to use Dy₂O₃ as the insulating material in a FET-like configuration in which the carrier concentration and transition temperature are controlled by a metal gate.

An account of this work was presented at the Applied Superconductivity Conference and has been published in its proceedings (Beauchamp, 1991). A more detailed discussion of these results was published in the *Journal of Materials Research* (Zhang, et al., 1992).

2. Lithographic Patterning and Growth of DyBaCuO on Si Substrates

This research is directed at the development of the capability to grow films using ozone-assisted MBE directly onto Si substrates, and to develop unique procedures involving the use of Si contact masks to lithographically pattern high- T_c films. Both activities share the common technical problem of determining the conditions under which high- T_c superconductors grow, or will not grow on Si, or SiO substrates. This approach to lithography has the advantage that all processing steps involving fabrication are carried out in Si technology.

We have successfully grown films of DyBa₂Cu₃O_x in situ on Si at low substrate temperatures ($\sim 640^{\circ}$ C) by MBE using O₃ as a source of activated oxygen. The best film thickness 2300 Å was found to be highly c-axis oriented having a resistive transition onset at 90 K and zero resistance by 70 K. Transmission electron microscope pictures of this film show a 150 Å amorphous layer between the Si substrate and the high-T_c film. Auger electron spectroscopy (AES) depth profiles show 400 Å of interdiffusion and an increase of Ba in this layer when oxidized Si is also present. The results of this study have been published in the *Journal of Applied Physics* (Nordman, et al., 1991).

The idea associated with the lithography using Si masks is that except under special conditions, high-T_c films will not grow on Si substrates. Consequently, if one were to overlay a SrTiO₃ substrate with Si, and then pattern the Si to form open channels, a deposited film of the high-T_c material would only form with the correct stoichiometry and crystal structure in the space of the channels. If one were to lithographically pattern submicron or nanometer scale channels, then the resultant film structure would consist of wires with those dimensions. The material deposited onto the Si contact mask would presumably be amorphous, insulating and nonsuperconducting. The complication is that high-T_c films can grow on Si, so that one must be very careful to select growth conditions which produce nonsuperconducting layers on the contact mask area and superconducting films in the open spaces defined by the channels. We have been carrying out systematic studies of growth conditions so as to be able to control this process and thus routinely pattern high-T_c superconducting films using the above procedure. This work is continuing under a new AFOSR grant.

3. Conventional Microelectronic Patterning

Efforts to study multilayered films or fabricate superconducting devices require a patterning method which defines the needed structure and allows electrical contact to the various buried

layers. Our current process involves optical lithography and ion milling to pattern $YBa_2Cu_3O_x$ (YBCO) films and $YBCO/Y_2O_3$ multilayers. The approach can be used with other multiple layer structures and other materials. Line widths and structure dimensions of 2 to $10\mu m$ are possible. Electrical contact to the small structures is facilitated by patterning a metal layer to form an interconnect between the structure and a larger pad to which a conventional wire bond can be made. The remote contact lines are overlaid on an insulating layer of oxidized yttrium which protects the sidewalls of the patterned structure and isolates the contact from the other layers. The process has been used to define small mesas suitable for testing SIS planar tunnel junctions. The implications of the method are many since it enables contact to SIS and SNS structures, which are the basis of many superconducting devices, and it allows testing of other multilayer structures.

4. Initial Growth Stages of Ultrathin Films

We have carried out studies of the effect of substrate structure on the initial stages of nucleation and growth of ultrathin DyBaCuO films. The substrates themselves have been studied using X-ray diffraction k-space mapping. Needless to say this has resulted in our ability to ascertain the quality of the product offered by various vendors. It is clear that an unappreciated aspect of obtaining film quality is substrate quality as several popular vendors actually supply very low quality material. The techniques used to study film growth in detail have thus far have been AFM, TEM, and XRD. Our results to date are summarized below.

Heterogeneous nucleation at surface irregularities predominates and appears to result in island growth, to the resolution of the techniques used. Surface roughness on unreconstructed substrates is the order of 1 to 2 nm over a length scale of 200 nm. Reconstruction increases the surface roughness by a factor of 2, thus providing a higher density of nucleation sites. Reconstructed surfaces of (100) and (110) substrates are different as are the growth morphologies of the films. Growth on (100) appears to be consistent with an island mode of growth rather than the Stranski-Krastanov mode, as thought earlier. The (110) substrate orientation exhibits hills and valleys, running along (111) crystallographic directions. Islands of DyBaCuO line up along these. Increase of film thickness increases the density of islands, the island size saturating at about 50 nm. The critical size of a nucleus of DyBaCuO is about 2 to 5 nm. The growth appears to be some kind of diffusion limited aggregation. Misfit dislocations are observed in the form of Moire contrast at film thicknesses of 100 nm. The critical thickness for misfit dislocations is estimated to be in the range 30-50 nm, depending upon the epitaxial relationship considered for SrTiO3 substrates. This research is currently being pursued in detail supported by a new AFOSR grant.

5. Controlled Film Growth and Film Characterization

An important milestone in this thin film growth effort, which is the basis for the new AFOSR grant, was the delivery of a new film deposition system by Perkin Elmer Corporation in January 1990. The major problems associated with making this system operational have been solved. The vendor had difficulties in making the substrate heater perform to specifications without burning out, and the reflection high energy electron diffraction (RHEED) system initially did not work at all. Both of these problems have been solved.

The main focus of our efforts has been on the establishment of the highest degree of control possible of all facets of the growth process. To this end we have upgraded the controllers for the Knudsen cells, and examined in detail the interaction of evaporants with various crucible materials. A significant advance has been the observation of RHEED oscillations during film growth of high-T_c films. Different schools of thought exist about such oscillations. Some believe that they are associated with layer growth with a period corresponding to the time required for the completion of a layer. Other approaches attribute the oscillations either to the formation of steps, where the growth is by propagation of steps, or to configuration dependent reactive incorporation of gaseous

species, which in this instance would be ozone. The observation of such oscillations would seem to make possible layer-by-layer engineering of structures, which would increase the range of structures available for investigation.

To produce high-quality films or structures, one starts with well-characterized substrates. Then considerable time and effort must be spent on attaining reproducibility of growth parameters, and understanding the basic phenomena that govern the nucleation and growth. Only with such a sound base of knowledge is it possible to achieve reproducibility and progress towards fabrication technology for devices. We have developed such a knowledge base for the operation of our MBE system.

We have, as described above, established the influence of substrate surface structure as an important parameter affecting the microstructure of films by provision or lack thereof of nucleation sites (Agrawal, et al., 1992). This variable is also found to influence the epitaxial relationship, when more than one epitaxial orientation is possible, through local variations in supersaturations. Growth occurs by step propagation, and is well described by a step flow model (Chandrasekhar, et al., 1992a). This type of a growth mechanism can be exploited to yield relatively flat planar layers, with steps, on which further growth can be done in order to obtain planar tunnel junctions. Use of vicinal substrates exploits this mode of growth to great advantage, and presently studies are being conducted on this aspect. Extension of the step flow model predicts the observed spiral morphology of the grains quite well. RHEED has been used as an in situ technique for the study of film growth. Our observation of RHEED oscillations and spiral morphology simultaneously, indicates that contrary to popular belief, atomic scale smoothness is not a requirement for RHEED oscillations (Chandrasekhar, et al., 1992b).

We have also found that the RHEED oscillations themselves are not indicative of layer-by-layer growth, but the oscillations do contain useful information about the evolving microstructure, if interpreted with care. We have also established that claims of superconductivity in one unit cell thick films (Terashima, et al., 1991) are open to question (Chandrasekhar, et al., 1992c, 1992d). The RHEED oscillations arise from modulations in surface roughness of the growing film. These oscillations have been found to exhibit surface diffusion-dominated behavior, the time period as well as the amplitudes being substrate temperature dependent, despite the fact that MBE is a regime of complete condensation (Achutharaman, et al., 1992). Thickness control is better achieved by monitoring fluxes rather than RHEED oscillations, under such circumstances.

The recent acquisition of a LEED system will permit further quantitative evaluation of substrate surface step distributions and determination of their influence on film microstructure. This should enable us to design structures using the stable substrate surface structure as a controlled variable, which acts as a template, rather than relying substrate surface temperature by itself. The effect on nucleation of having either an A-rich or a B-rich substrate surface for ABO₃ type substrates commonly used to grow high-T_c thin films is being explored.

Recently a Philips X-ray diffractometer equipped with a 4 crystal monochromator for low beam divergence, was acquired. The sample sits on an open Eulerian cradle and the diffractometer itself is capable of being operated either in the parallel beam mode or the high resolution mode. A further option is the use of a 3-axis goniometer, with an analyzer crystal near the detector, used in the parallel beam mode. The monochromators are Ge crystals, and can be switched from the 220 to the 440 reflection for sensitive work. This diffractometer affords unsurpassed capabilities for the structural analysis and characterization of substrates, films and structures. X-ray reflectance measurements yield information on substrate and film quality. The Eulerian cradle permits the determination of volume fractions of a certain epitaxial relationship, and the 3-axis system permits high resolution measurements to be made in reciprocal space. This capability has enabled us to reduce the turnaround time for X-ray analysis, and obtain quantitative information about the effect of process variables on film microstructure.

An RF ion source with a plasma bridge neutralizer which enables us to reproducibly prepare substrates for deposition has been recently installed in the MBE system. This configuration will minimize substrate surface charging and damage by the impact of multiply ionized atoms. This is an important aspect to be borne in mind while growing ionic compounds on insulating substrates, an unavoidable feature of high-T_c thin film growth. Use of the ion source during deposition will permit the planarization of surfaces and the subsequent elimination of outgrowths, which will short out planar tunnel junctions. For tri- and multi-layer structures, the planarization of the substrate, the film, or the barrier layer, or all of them would appear to be critical. The RHEED can be used to monitor the planarization with an increase in specular intensity indicating a more planar surface. The capability to operate the ion source with oxygen ensures that an oxygen rich environment is maintained in the vicinity of the oxide superconducting films, thereby minimizing the possibility of obtaining a dead layer and the problems associated with measurements on such layers, and devices incorporating them. Using the in situ electron beam evaporation source it will be possible to fabricate in situ contact layers for films as well as tri- and multi-layer structures. This technique yields contacts with resistivities in the 10-7 to 10-8 range.

As mentioned above, we have developed the capability to grow more than one type of superconducting compound and several different insulators. Presently we can grow either the La₂CuO₄ family of compounds or the (RE)Ba₂Cu₃O_{7-\delta} family of compounds, where RE=Y or Dy. The insulators which have been grown are (RE)₂O₃ with RE = Y or Dy, Sr TiO₃ and La₂CuO₄. The latter is the insulator from which LaSrCuO is derived by doping. This compound, due to its tetragonal symmetry, is in our view, a better choice as a barrier material than the (RE)₂O₃ type compounds, which due to their cubic symmetry and isotropy, tend to agglomerate on any surface when grown. The tetragonal compound on the other hand, due to its anisotropy, tends to remain planar. The compound is truly insulating, in contrast with PrBa₂Cu₃O_{7-\delta}, which is a semiconductor with significant conductance.

The various materials mentioned above are potential building blocks of various devices and structures involving high- T_c superconductors. The primary issue for all possible structures is whether combinations of these various films can be grown epitaxially, with interfaces between the layers microscopically ordered and sharp on an atomic scale. A secondary issue is whether the interfaces are free of defect states of various types which can serve as traps for carriers. The latter condition would be important for the functioning of FET-like devices. Finally, any combination of layers would have to be patterned in a manner which did not degrade the structures and influence performance, and which permitted electrical contact to be made in a controlled manner.

It is important to realize that the literature is replete with claims of isolated layers, or perfect multilayers. Various analytical procedures indicate that such claims are not correct, and that multilayer structures which have been produced are characterized by substantial interlayer diffusion, and so-called layer-by-layer growth in actual fact does not occur. Thus, attempts to fabricate structures will have to employ strategies for living with the realities of film growth. Our philosophy has been to attempt to produce planar configurations of films where different device properties result from different thicknesses of various layers, or different materials from our catalog of compatible materials. The approach requires control over the orientation of crystallites in the film so as to optimize performance in a given application. For instance, it may be desirable for tunneling to be in the c-direction for some SIS junction configurations, but would certainly have to be in the a- or b-directions for Josephson devices. Control of crystalline orientation could involve the use of oriented substrates, subtle changes in stoichiometry, or substrate temperature during growth.

C. Electrical Noise Studies

This work grew out of a DARPA-funded project under a subcontract from Honeywell. Honeywell has supported the study of noise in bolometers. We have extended this effort under the AFOSR Grant to include research on films grown on more conventional substrates. The effort may turn out to be an important probe of the glass transition in high-T_c superconductors, an important matter relating to critical currents in a magnetic field.

Voltage noise power spectral density measurements as a function of temperature, frequency, current, and magnetic field on DyBa₂Cu₃O_{7-x} (DBCO) thin films have been proceeding. The goals has been to understand the "intrinsic" noise present in DBCO thin films grown on SrTiO₃ or LaAlO₂ substrates, namely: the occurrence of a peak in the excess spectral density at the foot of the resistive transition in the presence of a magnetic field.

We have shown that the magnetic field applied parallel to the c-axis plays an important role in determining the magnitude and spectral dependence of the voltage noise peak. A high field apparatus was constructed to study this field dependence up to 8 Tesla using a conventional four-probe technique employing a constant current. Recent results indicate that at kilogauss fields the spectral density has a highly distinctive frequency dependence. A corner, or kink, is clearly visible in the frequency dependence. For frequencies above this corner frequency, the spectral slope is steeper than 1/f whereas for frequencies below this corner frequency the spectral slope is much shallower than 1/f. Current, temperature, and small perturbations of the magnetic field can shift the position of this corner frequency, as well as the magnitude of the spectral density, in controllable and reproducible ways. Preliminary studies of the temperature dependence of the corner frequency indicate that it may be of Arrhenius form with a temperature dependent activation energy. Further careful measurements are being carried out in order to quantitatively study this feature in the context of various models concerning themselves with the phase diagram.

D. Optical Effects

In collaboration with A. J. Heeger's group at the University of California at Santa Barbara, we have been studying "photo-doping" of semiconducting ultrathin epitaxial films of $DyBa_2Cu_3O_{7-x}$ to the metallic state. There is evidence of an effect, in that at light intensities in excess of $5x10^{15}$ photons.cm² the activation energy of the temperature-dependent resistivity approaches zero and a minimum appears below 100 K. A modest longitudinal magnetic field (< 0.5 Tesla) reduces both the resistivity minimum and the transient contribution to the conductivity. (See Yu, et al., 1992).

E. Hemispherical Target Sputtering

In collaboration with G. Wehner of the Electrical Engineering Department, high quality stoichiometric films of YBa₂Cu₃O_{7-x} were also grown using a unique sputtering technique involving the use of a stoichiometric target of hemispherical shape (Wehner, et al., 1988). This was done in a Hg vapor triode plasma. The method permits the fabrication of stoichiometric films from stoichiometric targets. This process has the advantage that simple modifications will permit significant increases in sputtering rates and the process can be scaled up in size easily. The use of a spherical target in effect permits an averaging over the angular distribution of the sputtering yield of the constituents. The method was also extended to include spherical targets (Wehner, et al., 1989).

F. Magnetic Studies of Bulk High-T_c Superconducting Materials

These investigations were carried out using a Quantum Design Superconducting SQUID Susceptometer. The first work involved the investigation of the time dependence of the magnetization of polycrystalline samples of YBCO (Tuominen, Goldman and Mecartney, 1988a). A comparison of field-cooled and zero field-cooled magnetizations revealed the existence of a reversibility line. A logarithmic dependence of the decay of the field-cooled magnetization was observed. The temperature dependence of the fractional change of the magnetization was observed to have a peak. This first work was interpreted in the context of a superconducting glass model. It is clear at this time that a critical state model would also work. It was later found that similar results could be obtained from the study of single-crystals samples of YBa₂Cu₃O_{7-x} (Tuominen, Goldman and Mecartney, 1988b).

Research on magnetic properties then turned to the question of magnetic anisotropy. The anisotropies of Bi₂Sr₂CaCu₂O_y and YBa₂Cu₃O_{7-x} were investigated by simultaneously measuring the longitudinal (M_L) and transverse (M_T) components of the equilibrium magnetization of crystals oriented at arbitrary angles with respect to the applied field direction (Tuominen, et al., 1990a). The variations of M_L and M_T as a function of orientation, field and temperature were measured. In the regime in which the simple three-dimensional anisotropic London theory is valid it was shown that the ratio of the two magnetizations yields the anisotropic effective mass ration m₃/m₁ directly. This number was found to be 30 and 280 for crystals of YBa₂Cu₃O_{7-x} and Bi₂Sr₂CaCu₂O_y respectively.

The same apparatus was then used to study the relaxation of the longitudinal and transverse components of the remanent magnetic moment of single crystal Bi₂Sr₂CaCu₂O_y as a function of angle (Tuominen, et al., 1990b). When the angle between the applied field and the c-axis is not too large, the remanent moment aligns quickly with the c-axis. At extremely high angles this alignment process is slow and at low temperatures the transverse magnetization even increases with time. The temperature dependence of the normalized relaxation rate exhibits two peaks, suggesting the existence of two separate pinning mechanisms.

G. Electrical Transport in TlBaCaCuO Thin Films

This work was carried out in collaboration with a former student, J. Kang, who at the time was a postdoc at Argonne National Laboratory, and is now a staff member at Westinghouse. The first studies involved measurements of in-plane fluctuation-enhanced conductivity of c-axis oriented TlBaCaCuO thin films performed over the temperature range from T_c to 240 K (Kim, et al., 1989a). The results were consistent with two-dimensional fluctuation theory and with a linear dependence of the normal state resistivity on temperature down to $(T-T_c)/T_c$ the order of 0.03. A crossover to three-dimensional fluctuations close to T_c was not found. The width of the superconducting transition appeared to be a measure of a distance over which layers fluctuate in a correlated manner.

The transport properties of the same type of films were then examined within the context of the Kosterlitz-Thouless-Berezinskii model (Kim, et al., 1989b). The nonlinear current versus voltage and resistivity versus magnetic field characteristics below the transition temperature together with the exponential inverse-square-root temperature dependence of the resistivity just above T_c were consistent with each other and with the theory. The parameterization of the resistivity data using the Aslamazov-Larkin theory well above the KTB transition was consistent with that of the KTB theory in the transition region.

H. Other Work

In the early days of high-T_c superconductivity, X-ray photoelectron spectroscopy studies were performed on bulk polycrystalline samples of YBCO as a function of temperature through the superconducting transition (Kim, et al., 1988). With decreasing temperature, clear changes were observed in the photoelectron spectrum which were at the time interpreted as signatures of the Cu³⁺ and perhaps the Cu¹⁺ oxidation states, in addition to the usual Cu²⁺ state. These changes were not observed in samples which had been rendered nonsuperconducting by baking in vacuum.

The fabrication of superconductors using sol-gel synthesis was also investigated (Accibal, et al., 1989). A comparison of the use of three different coordination compounds of copper as precursors for the sol-gel synthesis of YBa₂Cu₃O_{7-\delta} has been made. For yttrium, the tris(isopropoxide) was used exclusively, while the use of both Ba(O-i-Pr)₂ and Ba(OCH₂Ch₂OEt)₂ (prepared in situ from Ba metal) as sources for Ba were studied. After dissolving Y(O-i-Pr)₃, a Ba source, and the copper(I) alkoxide, [Cu(O-t-Bu)]₄, hydrolysis led immediately to an orange gelatinous solid which yielded YBa₂Cu₃O_{7-\delta} upon firing in oxygen. Copper(II) acetate was found to give heterogeneous mixtures under our conditions and was not further studied. Copper(II) acac (acac = acetylacetonate) yielded the best results. Partially hydrolyzed solutions of Cu(acac)₂, Ba(OCH₂CH₂OEt)₂, and Y(O-i-Pr)₃ were spin coated on SrTiO₃ (100) and fired under oxygen to give oriented (b axis normal to the surface) thin films of YBa₂Cu₃OO_{7-\delta}. The onset of superconductivity for the films was 92 K, but they did not reach zero resistance until much lower temperatures.

III. PERSONNEL

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V. PATENTS

"Preparation of Superconductive Ceramic Oxides Using Ozone," U.S. Patent No. 5,039,657, Dated August 13, 1991

VL DISSERTATIONS

A. Doctoral

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 Present Employer: Argonne National Laboratory (K. Gray)
- Berkley, D. D., "In situ Preparation of Y-Ba-Cu-O Superconducting Thin Films Using Pure Ozone Vapor Oxidation," December 1989
 Present Employer: Naval Research Laboratory (S. Wolf)
- Tuominen, M., "Anisotropic and Time-Dependent Magnetization of the High Transition Temperature Superconducting Cuprates," July 1990 Present Employer: Harvard University (M. Tinkham)
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B. Masters

- Hassler, B. A., "High T_c Superconducting Thin Films by Sol-Gel Coating," December 1988 Present Employer: Medtronics, Inc.
- Agrawal, Vijay, "Initial Stages of Epitaxial Growth of Dysprosium Barium Copper Oxides Films on Strontium Titanate Substrates," June 1992

 Present Employer: Department of Electrical Engineering, University of Minnesota